P78

Effect of the hydrophilicity degree of silicon substrate on the morphology of the triglycine film

A.S. Morozova[1, 2], S.A. Ziganshina[1], A.A. Bukharaev[1], M.A. Ziganshin[2]

[1]*Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center of RAS, 420029, Kazan, Russia morozova_anna_s@mail.ru*

[2]*Kazan Federal University, 420008, Kazan, Russia*

The influence of silicon substrates with different surface properties on the self-organization of tripeptide based on glycine in the film was studied using atomic force microscopy.

The formation of organic crystals and studying of their properties are among the actual problems of nanotechnology [1]. Wherein the methods for producing of micro- and nanocrystals with physicochemical properties determined by the surface morphology are being actively developed [2]. One of the methods for formation of organic crystals is the self-assembly of amorphous films deposited on various substrates after interaction with the vapors of organic compounds. Variation of organic vapors or substrate type allows to obtain organic structures with different geometric parameters [3]. At the same time, the directed self-assembly of molecules in thin films and predicting the possible morphology of the film surface and crystals grown is still a challenge [4].

The popular objects for such studies are the oligopeptides, since micro- and nanostructures based on them are currently used in various technologies [5]. A feature of oligopeptides is the ability to self-assemble with the formation of various structures [6]. The simplest oligopeptide from the variety is the dipeptide glycylglycine, formed from the residues of the simplest amino acid – glycine. Glycine being a part of many proteins and biologically active compounds has a high biological activity [7], so the structure and properties of its crystals are rather well studied [8]. But the properties of glycine-based oligopeptide crystals have not been sufficiently studied. Di- and triglycine are of great interest in connection with the possibility of their use in the production of biologically active and medicinal drugs [9].

Earlier we found that the nature of the substrate has a significant effect on the morphology of the initial film of tripeptide (glycyl-glycyl-glycine, GGG) [10], as well as on the morphology of the films after the interaction with organic vapor.

In the present work, the attempt to evaluate the effect of the hydrophobicity degree of silicon substrate on the morphology of GGG film before and after interaction with vapors of organic compounds and water was made. For creation of the silicon surface with hydrophobic properties a special treatment of hydrophilic silicon with a 5% solution of hydrofluoric acid for 40 minutes was used.

Films on the substrate surface were formed by dropping of the freshly prepared tripeptide solution (40 μl, 1 mg/ml) in a methanol/water mixture followed by solvent evaporation. The extended crystals of GGG on the surface of hydrophilic silicon after spontaneous evaporation of the solvent were formed. The dendrite-like structures of GGG are formed on hydrophobic silicon. Apparently, the crystal structure of silicon promotes the self-assembly of the GGG film with the formation of crystalline structures. On the surface of silicon plate there are oxides and hydroxyl groups which are capable to effective adsorb of the tripeptide molecules. These groups also can orient the GGG molecules in space through interaction with charged carboxylate ($-COO^-$) and ammonium ($-NH^{3+}$) groups which are in the plane (001) of the GlyGly crystal.

To study the process of self-assembly and the formation of nanostructures and crystals with different shapes and sizes, it is necessary to obtain amorphous films on the surface of the substrates. Since the amorphous films, being metastable from the point of view of thermodynamics, possess excess energy and can be transferred to an ordered state (nanostructures, crystals) under the influence of external factors [11]. Therefore, a technique for producing an amorphous GGG film by quickly evaporation of the solvent was developed.

The saturation of films by the organic compounds vapors (alcohols, chloroform, dichloromethane, benzene, acetonitrile, pyridine) and water was carried out for 2-3 hours at room

temperature. It was found that only strong protonodonors (alcohols) and protonacceptor (pyridine) affect the GGG film deposited on hydrophilic silicon. Well-cut rectangular crystals were found on the surface. The results obtained show that hydrophilic silicon prevents the formation of structures on the surface of the amorphous GlyGly film under the interaction with weak (dichloromethane, chloroform, acetonitrile, benzene) protonodonors and protonacceptor. In this case, the properties of hydrophilic silicon are similar to those of mica. The morphology of the film deposited on hydrophobic silicon was changed by both strong (alcohols, water and pyridine) and weak (dichloromethane, chloroform, acetonitrile, benzene) protonodonors and protonacceptors. For example, the action of dichloromethane vapors on the GG film deposited on hydrophobic silicon leads to the formation of small, interconnected, crystalline structures. In this case, the properties of hydrophobic silicon are similar to those of highly oriented pytrolytic graphite.

Thus, the paper demonstrated the influence of the hydrophilicity degree of a silicon substrate on the surface morphology of GGG films after interaction with vapors of organic compounds.

The results obtained can be useful in developing methods for the controlled assembly of short-chain peptides on solid surfaces by rational choice of substrate and vapor or for explaining the reasons for the formation of various shapes nanostructures based on short peptides when different substrates are used.

1. X. Yang, A.S. Myerson, *Cryst. Eng. Comm*. **17**, 723 (2015).
2. J. Li, C.J. Tilbury, S.H. Kim, M.F. Doherty, *Progress in Materials Science* **82**, 1 (2016).
3. J.S. Lee, J. Ryu, C.B. Park, *Soft Matter* **5**, 2717 (2009).
4. F. Punzo, *J. Molecular Struct.* **1032**, 147 (2013).
5. S. Kim, J.H. Kim, J.S. Lee, C.B. Park, *Small* **11**, 3623 (2015).
6. M. Zelzer, *Chem. Soc. Rev.* **39**, 3351 (2010).
7. Y. Lu, X. Zhu, J. Li, *Biochemical Pharmacology*. **123**, 40 (2017).
8. V. Vijayalakshmi, P. Dhanasekaran, *J. Cryst. Growth*. **506**, 117 (2018).
9. M. Liakopoulou-Kyriakides, *Studies in Natural Products Chemistry* **27,** 793 (2002).
10. А.С. Морозова, С.А. Зиганшина, А.А. Бухараев, М.А. Зиганшин, *Труды XXIII Международного симпозиума «Нанофизика и наноэлектроника» 11–14 марта 2019 г., Нижний Новгород*. **1,** 373 (2019).
11. P.G. Debenedetti, F.H. Supercooled, *Nature* **410**, 259 (2001).